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Meijerink, Marc; van Mastrigt, Frank; Franken, Linda E.; Stuart, Marc C. A.; Picchioni, Francesco; Raffa, Patrizio

Published in:
Pure and Applied Chemistry

DOI:
[10.1515/pac-2016-1021](https://doi.org/10.1515/pac-2016-1021)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Meijerink, M., van Mastrigt, F., Franken, L. E., Stuart, M. C. A., Picchioni, F., & Raffa, P. (2017). Triblock copolymers of styrene and sodium methacrylate as smart materials: synthesis and rheological characterization. *Pure and Applied Chemistry*, 89(11), 1641-1658. <https://doi.org/10.1515/pac-2016-1021>

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Conference paper

Marc Meijerink, Frank van Mastrigt, Linda E. Franken, Marc C. A. Stuart,
Francesco Picchioni and Patrizio Raffa*

Triblock copolymers of styrene and sodium methacrylate as smart materials: synthesis and rheological characterization

DOI 10.1515/pac-2016-1021

Abstract: Well-defined amphiphilic triblock poly(sodium methacrylate)-polystyrene-poly(sodium methacrylate) (PMAA-*b*-PS-*b*-PMAA) copolymers characterized by a different length of either the hydrophilic or the hydrophobic block have been synthesized by ATRP. In solution the micelle-like aggregates consist of a collapsed PS core surrounded by stretched charged PMAA chains. The micelles are kinetically ‘frozen’ and as a consequence the triblock copolymers do not show a significant surface activity. The hydrophilic block length has a major influence on the rheology, the shortest PMAA blocks yielding the strongest gels (at the same total weight concentration). The hydrophobic block length has only a minor influence until a certain threshold, below which the hydrophobic interactions are too weak resulting in weak gels. A mathematical model is used to describe the micelle radius and the results were in good agreement with the experimentally found radius in transmission electron microscopy. The influences of the ionic strength, pH and temperature on the rheology has also been investigated, showing the potential of these polymers as smart hydrogels. The change in conformation of the hydrophilic corona from the collapsed state to the stretched state by changing the pH was quantified with zeta-potential measurements. To the best of our knowledge, this is the first systematic investigation of this kind of triblock copolymers in terms of their rheological behavior in water.

Keywords: amphiphilic block copolymers; ATRP; cryo-electron microscopy; POC-16; rheology; smart hydrogels; zeta potential.

Introduction

Amphiphilic block copolymers are of great industrial importance due to their adjustable rheological behavior and formation of self-assembled structures in a selective solvent like water [1, 2]. The possibility exists to introduce responsive behavior to parameters such as pH [3–5], temperature [6, 7] or UV irradiation [2]. The versatility in properties has resulted in an increased attention in the last decades for application in several fields including smart materials [6, 7], micro emulsion stabilization [8] and polymerization [9, 10], coatings [11], drug delivery [12–14] and enhanced oil recovery [2, 3, 15, 16].

Amphiphilic block copolymers are tunable in terms of both rheology and interfacial properties. Subsequently, they can be considered as the macromolecular counterparts of small-molecule surfactants and

Article note: A collection of invited papers based on presentations at the 16th International Conference on Polymers and Organics Chemistry (POC-16), Hersonissos (near Heraklion), Crete, Greece, 13–16 June 2016.

***Corresponding author: Patrizio Raffa**, Department of Chemical Engineering – Product Technology, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, Tel.: +31(0)503634465, e-mail: p.raffa@rug.nl

Marc Meijerink, Frank van Mastrigt and Francesco Picchioni: Department of Chemical Engineering – Product Technology, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Linda E. Franken and Marc C. A. Stuart: Electron Microscopy Group, Groningen, Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands

are therefore also called polymeric surfactants [2, 17]. Amphiphilic block copolymers can be synthesized with a large variety of monomers [2] and architectures [18, 19], which determine their aggregation behavior in water. In the case of a short hydrophobic and a long polyelectrolyte block the copolymers form star-like polyelectrolyte micelles [20]. The use of a polyelectrolyte such as PAA or PMAA in the block copolymer is particularly interesting because the charges on the backbone give repulsive electrostatic interactions, which lead to a highly stretched conformation [21]. The rheological properties of a block copolymer solution are mainly derived from the inter-micellar interactions, which in turn derive from chemical nature, length and tacticity of the hydrophilic blocks, whereas the interfacial properties derive from the intrinsic molecular structure of the polymer [22, 23]. The rheology of diblock PS-*b*-PAA and PS-*b*-PMAA in water has been widely studied [24, 25], but a systematic study of rheological properties of their triblock copolymers is still missing. The aggregates of the diblock PS-*b*-PAA constitute of a dense rigid PS core surrounded by a hydrophilic corona of PAA brushes. Rheological studies show that amphiphilic block copolymers form viscoelastic solutions and turn into gels after a critical concentration [26, 27].

The dynamic nature of the aggregates formed by amphiphilic block copolymers is an interesting research topic. Observations indicate that these block copolymers often behave as kinetically “frozen” micelles [28, 29]. In literature it is described that amphiphilic block copolymers display very low diffusion coefficients. Subsequently equilibrium situations between the unimers and micelles are reached only after a very long period of time [18, 30]. In particular the high hydrophobicity and glass transition temperature of polystyrene causes a large activation energy barrier for molecular exchange and does not allow restructuring of the aggregates [31]. These observations were made for diblock and triblock copolymers of PS and PEO [30], diblock copolymers of PS and PAA [32] and diblock copolymers of PS and PMAA [28].

The slow dynamic equilibrium between unimers and micelles in solution results in very low surface activity. However some studies propose that the system can be dynamic if the hydrophobic block is short enough, [27, 33] which makes it interesting to study the aggregation and properties of amphiphilic block copolymers with short hydrophobic blocks. Nevertheless, the absence or an extreme low CMC is advantageous for many applications, since only traces of polymer are required to form micelles.

Although many papers document the synthesis and self-assembly of amphiphilic block copolymers, to the authors best knowledge, only relatively little work has been carried out on the systematic study of the rheology, gel structure and surface properties of such polymers [2]. The field of polymeric surfactants is relatively new and a full understanding of the relation between structure and property is still missing. In this work, we present a systematic investigation concerning the rheological behavior of a series of amphiphilic PMAA-*b*-PS-*b*-PMAA triblock copolymers with different lengths of hydrophilic and hydrophobic blocks prepared by ATRP. Following our previous work [23] on PS-*b*-PMAA diblock copolymers, we set out to systematically investigate the influence of the copolymer structure on the final product properties. It is expected that a change of architecture (triblock instead of diblock) of the block copolymer has a certain effect on the rheological and interfacial properties. Also, shorter PS blocks were targeted in order to possibly observe a more dynamic system. Moreover, the rheological behavior of the triblock copolymer solutions at different temperatures, pH and concentrations of NaCl has been studied. The rheological properties change dramatically due to the screening effect of the salt which results in a collapsed conformation of the hydrophilic corona. The degree of electrostatic repulsion at different pH is quantified with zeta-potential measurements. Furthermore, the gel structure of the micelles in solution was investigated with cryo- and negative stain transmission electron microscopy.

Experimental

Materials

Tert-butyl methacrylate (tBMA, Aldrich, 98%) was vacuum-distilled over CaH₂ and kept under nitrogen before use. CuCl (Sigma-Aldrich, ≥99%) and CuBr (Sigma-Aldrich, ≥98%) were stirred in glacial acetic acid for 6 h,

then filtered, washed with acetic acid, ethanol, ethyl acetate and dried under vacuum before use. Styrene (Sigma-Aldrich, $\geq 99\%$) was filtered through a short column of basic alumina to remove inhibitors and then kept under nitrogen before use. Anisole (Sigma-Aldrich, anhydrous, 99.7%) was deoxygenated by bubbling with nitrogen for 60 min. N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), ethylene bis(2-bromoisobutyrate) (EBIB, Aldrich, 97%), tetramethylethylenediamine (TMEDA, Aldrich, $\geq 99.5\%$), and tris[2-(dimethylamino)ethyl]-amine (Me6TREN, Aldrich) were used as received, without further purifications.

Synthesis

The synthesis of PS-Br, PtBMA-*b*-PS-*b*-PtBMA and PMAA-*b*-PS-*b*-PMAA has been carried out as reported elsewhere [3].

Synthesis of polystyrene macroinitiator (PS-Br)

PS-Br macroinitiators were synthesized as follows: 1 mmol of initiator EBIB, CuBr (2 mmol), and styrene (20–50 mmol) were introduced under nitrogen in a 100 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser, previously purged with nitrogen. The mixture was further degassed by purging with nitrogen gas (N_2) for at least 45 min under vigorous stirring. After deoxygenation, the flask was put in an oil bath set to a temperature of 100 °C where after 1 min, TMEDA or PMDETA (2 mmol) was introduced under nitrogen to initiate the reaction. The solution turned light green as complex formation occurred and remained heterogeneous. After a given time, the reaction was stopped by cooling down, introducing air and diluting with around 50 mL of THF. The THF solution was filtered through a short column of basic alumina to remove the copper catalyst, then precipitated in a 20-fold excess of methanol. The precipitate was filtered, re-dissolved in THF, and re-precipitated in 2:1 v/v methanol/water, washed with methanol and dried overnight at 70 °C, affording a white solid. The conversion and the molecular weight were determined both gravimetrically and by GPC.

Synthesis of PtBMA-*b*-PS-*b*-PtBMA triblock copolymers

PS-Br macroinitiator (0.5 g), deoxygenated anisole (10 mL), the copper catalyst CuCl, and tBMA (according to stoichiometry) were introduced under nitrogen in a 250 mL round-bottomed flask equipped with magnetic stirring bar and reflux condenser, previously purged with nitrogen. The mixture was further degassed by purging with nitrogen gas (N_2) for at least 45 min under vigorous stirring (1050 rpm). After deoxygenation and complete dissolution of the macroinitiator, the flask was put in an oil bath at 90 °C and the ligand (Me6TREN or PMDETA) was added under nitrogen. After a given time, the reaction was stopped by cooling down, introducing air, and diluting with around 50 mL of THF. The THF solution was filtered through a short column of alumina to remove the copper catalyst, then precipitated in a 20-fold excess of methanol, re-dissolved in THF and re-precipitated in 2:1 methanol/water mixture twice, washed with methanol, and dried overnight at 70 °C, affording a white solid. The conversion and the molecular weight were determined both gravimetrically and by 1H -NMR (solvent $CDCl_3$).

Synthesis of PMAA-*b*-PS-*b*-PMAA triblock copolymers and their sodium salts

A certain amount of PtBMA-*b*-PS-*b*-PtBMA precursor (2 g) was dissolved in 100 mL dioxane in a 250 mL round bottomed flask equipped with a magnetic stirring bar and reflux condenser. The dissolution is quite slow at low temperatures, therefore the temperature was set on 100 °C. After complete dissolution, an excess of concentrated HCl (10 mL) was added. The solution turns from transparent to cloudy in about 1 h. After 3–4 h the reac-

tion was stopped by cooling after which the solution turns back to transparent. The solution was precipitated in an excess of acetone (1 L). The precipitate was filtered and dried overnight at 70 °C. The polymers were recovered as glassy transparent whitish solids. The extent of hydrolysis was determined by ^1H -NMR in d_6 -DMSO. The corresponding sodium salts were obtained by dissolving the polymer in an excess of NaOH in water. The excess base was removed by dialyzing against Milli-Q water, changing water at least three times over a period of 2 days. The polymer was dried at 70 °C for 3 days, obtaining glassy transparent white-yellowish solids.

Characterization

Rheology experiments

Rheological measurements were performed on a HAAKE Mars III (ThermoScientific) rotational rheometer using a 2 mL solution at 20 °C. The rheometer was equipped with a cone-and-plate geometry (diameter 60 mm, angle 2°). A trap for the solvent was used in order to avoid water evaporation during the experiments. Solutions at 0.1, 0.5 and 1.0 wt% concentrations were prepared by dissolving the triblock copolymer sodium salts in demineralized water, followed by stirring for at least 10 h before the measurement in order to get homogeneous solutions. All the prepared polymers were soluble in water in their sodium salt form without the need for co-solvents or heating. Viscosimetric measurements, such as shear viscosity and viscoelasticity measurements were performed with shear rate variations of 0.1–500 s^{-1} and frequency ranges of $6.37 \cdot 10^{-3}$ –15.92 Hz (0.04–100 rad/s), respectively. Prior, to all viscoelasticity measurements a stress amplitude sweep experiment was performed in order to establish the regime of viscoelastic response, the linear viscoelastic region (LVR). Hereafter, oscillation frequency sweep measurements were performed at constant stress.

NMR spectra

^1H NMR spectra in CDCl_3 and d_6 -DMSO were recorded on a Varian Mercury Plus 300 MHz spectrometer operating at room temperature.

GPC measurements

Samples for the PS-Br macroinitiator and the triblock copolymers were prepared by dissolving the polymers in THF (99+ %, extra pure, stabilized with BHT) at 10 mg/mL concentrations. The samples were filtered over a 0.45 μm PTFE filter prior to injection. GPC measurements for the PS-Br macroinitiator were performed with a HP1100 from Hewlett-Packard, equipped with three 300 \times 7.5 mm PLgel 3 μm MIXED-E columns in series. Detection was made with a GBC LC 1240 IR detector. The samples were eluted with THF at a flow rate of 1 mL/min at a pressure of 140 bar. The PDI and molecular weights were determined using the software PSS WinGPC Unity. GPC measurements for the triblock copolymers were performed at 30 °C (1 mL/min) using triple detection consisting of a Viscotek Ralls detector, Viscotek Viscometer Model H502 and Shodex RI-71 Refractive Index detector. The separation was carried out by utilizing a guard column (PLgel 5 μm GUARD, 50 mm and two columns PLgel 5 μm MIXED-C, 300 mm from Agilent Technologies). Data acquisition and calculations were performed using Viscotek OmniSec Software using a refractive index increment (dn/dc) from the samples. Molecular weights were determined based on an universal calibration curve generated from narrow dispersity polystyrene standards (M_w from 645 to 30 01 000 g/mol).

Transmission electron microscopy

Three microliter of each sample at 1 mg/mL was pipetted onto a glow-discharged copper grid covered with carbon film. Due to the viscosity of the samples obtaining a thin layer of sample proved difficult and various

repetitions of washing with miliQ water and 2% uranyl acetate solution were applied before letting the final stain layer rest for 30 s prior to blotting. Blotting was done with different types of paper, because of their varying absorbing properties. The grids were visualized with either of two microscopes. One is a Tecnai G2 20 Twin electron microscope (FEI, Eindhoven, The Netherlands), that was equipped with an LaB6 cathode, an UltraScan 4000 UHS CCD camera (Gatan, Pleasanton, CA, USA) and operated at 200 kV. The other is a Philips CM120 electron microscope (FEI, Eindhoven, The Netherlands) equipped with a LaB6 cathode, 4000 SP 4K slow-scan CCD camera (Gatan, Pleasanton, CA, USA) and operated at 120 kV. Micrographs were cropped and their levels, brightness and contrast were optimized in Adobe Photoshop CS6.

Cryo-transmission electron microscopy

Three microliter of entry 8 at 0.3 or 0.5 mg/mL was applied to a glow-discharged copper grid with holey carbon film (quantifoil 3.5/1) and plunge-frozen with a Vitrobot (FEI, Eindhoven, The Netherlands) in liquid ethane after blotting for 20 and 28 s, respectively. The specimen was then inserted into a cryo-transfer holder (Gatan model 626) and transferred to a Philips CM120 electron microscope (FEI, Eindhoven, The Netherlands) equipped with a LaB6 cathode, 4000 SP 4K slow-scan CCD camera (Gatan, Pleasanton, CA, USA) and operated at 120 kV using low-dose mode. Micrographs were cropped and their levels, brightness and contrast were optimized in Adobe Photoshop CS6.

Zeta-potential measurements

The size and zeta potential measurements were performed in a ZetaPALS zeta potential analyzer (Brookhaven Instruments Corporation) using phase analysis light scattering, to determine the electrophoretic mobility of charged, colloidal suspensions in an electric field. The particle size was measured by dynamic light scattering. The polymer samples were prepared in water with different pH by HCl. Prior to each experiment, the pH was measured on a UltraBasic Denver Instrument. The glass electrode was calibrated with buffer solutions of pH 4 and pH 7.

Surface tension

Surface tension was measured using the pendant drop method on a Dataphysics OCA15EC tensiometer equipped with a CCD video camera (752*582 pixels). A 1 mL syringe was attached to a needle with a capillary radius of 1.36 mm. The drop was measured on its maximum size. Two sets of three measurements were taken and then averaged. Graphically the critical micelle concentration (CMC) was obtained from the plot of the surface tension against the concentration by taking the line of best fit in two places and noting the concentration at the intersection.

Results and discussion

Synthesis and characterization

The synthesis of PS-Br, PtBMA-*b*-PS-*b*-PtBMA and PMAA-*b*-PS-*b*-PMAA has been carried out as reported elsewhere [3]. The synthesis of difunctional PS-Br macroinitiators was performed in bulk at 100 °C, using CuBr as catalyst and TMEDA or PMDETA as ligand. Chain extension with tBMA was performed in anisole at 90 °C, using CuCl or CuBr as catalyst and PMDETA or Me6TREN as ligands. The synthesis is sketched in Fig. 1. The results are summarized in a supporting information file (Tables S1 and S2).

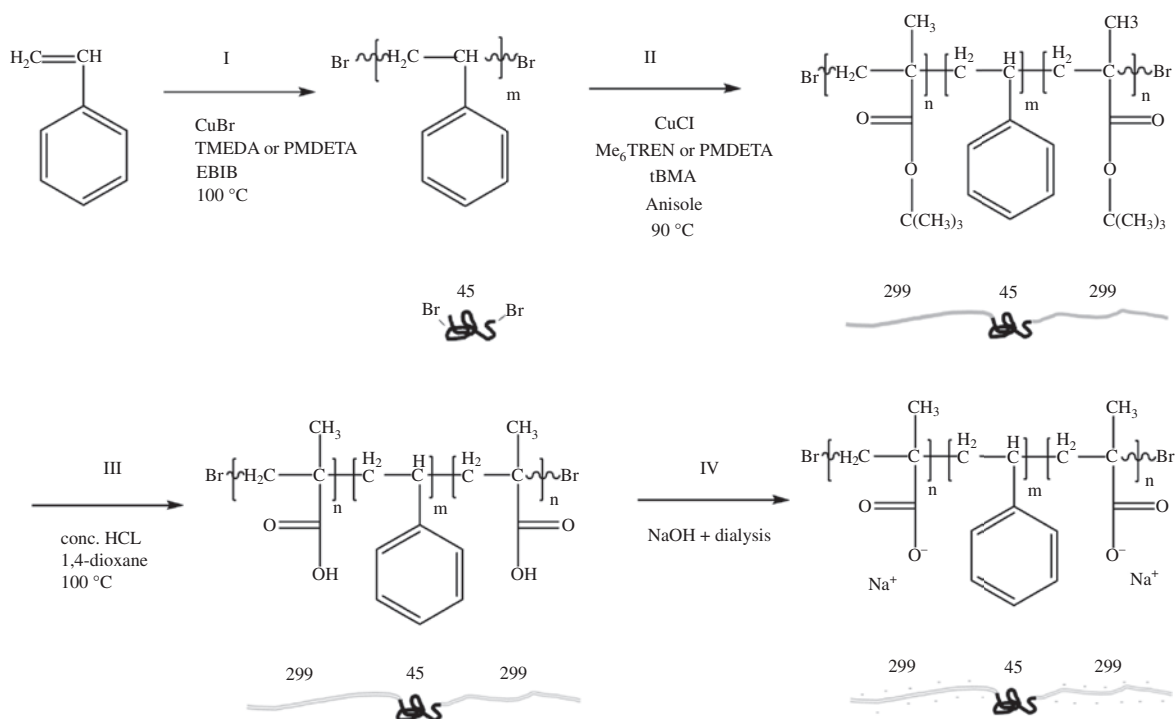


Fig. 1: Synthesis and structure of a polymer prepared in this publication (entry 11; PS45-PMAA598).

The final copolymers were characterized by ^1H -NMR and GPC. The molecular weight determined by conversion and ^1H -NMR were in good agreement and also comparable with studies by Davis et al. [34] and Raffa et al. [3]. The narrow molecular distributions obtained by GPC (Fig. 2) confirmed a successful chain extension and supports the fact that the ATRP polymerization is a controlled/“living” radical polymerization [35]. Figure 3 offers a graphical comparison between the relative sizes of the studied copolymer’s blocks.

The PS-PtBMA triblock copolymers have been selectively hydrolyzed with concentrated HCl in refluxing 1,4-dioxane, as reported previously [3, 23]. The primary ester groups in the difunctional initiator are stable in the adopted hydrolysis conditions [34, 36]. Hydrolysis was complete after 3 h, which was also confirmed by complete disappearance of the tBu peaks in ^1H -NMR (d_6 -DMSO) of the hydrolyzed products. After hydrolysis, the acidic form of the polymers was obtained, which does not dissolve in water but swells very slowly. The sodium salt of the prepared triblock copolymers was obtained after addition of NaOH. The excess base was removed by dialyzing the resulting solution in water for 3 days, refreshing water at least three times over a period of 2 days. The sodium salt form is readily soluble in water, forming clear colorless solutions with high viscosity.

Rheology

The rheological characteristics of the associated amphiphilic triblock copolymers were determined by shear viscosity and viscoelastic measurements of water solutions. The synthesized triblock copolymers possess interesting thickening capabilities. As demonstrated in Fig. 4, all the polymers solutions (1 wt%) are shear thinning whereas at lower shear rates ($\dot{\gamma} < 10 \text{ s}^{-1}$) most polymers reach an apparent Newtonian plateau with exception of entry 8 and 11, which have no apparent Newtonian plateau in the frequency range investigated except for diluted solutions of these polymers. The absence of a Newtonian plateau supports the fact that the amphiphilic block copolymers of entry 8 and 11 already form strong polyelectrolyte gels [24]. The shear viscosity profiles of the solutions can be fit with a power-law fluid model ($\eta = K\dot{\gamma}^{n-1}$) and provides an n value

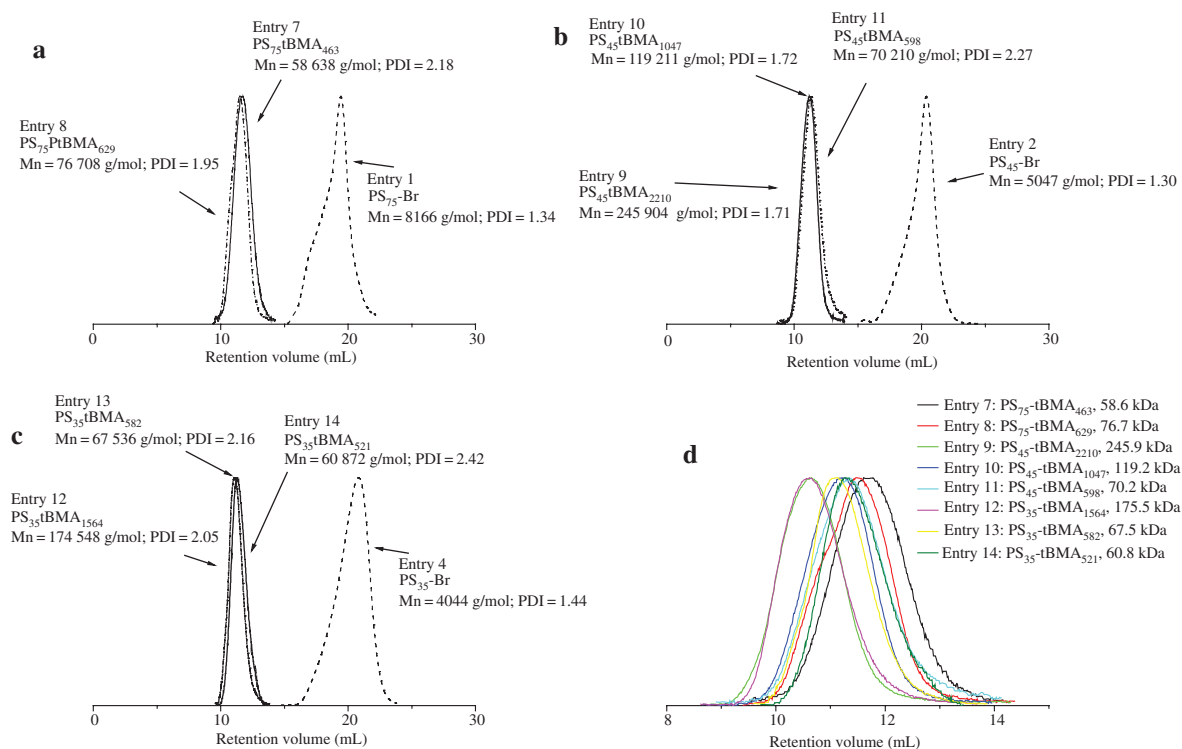


Fig. 2: Evolution of the molecular weight distributions for tBMA ATRP polymerizations using PS-Br macro initiator entry 1 (a), entry 2 (b) and entry 4 (c) as initiator and ME6TREN as ligand. (d) The GPC traces for the molecular weight distribution of the produced PS-tBMA triblock copolymers.

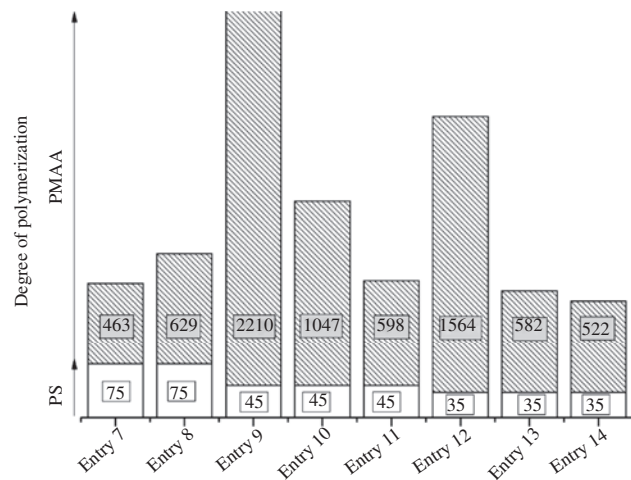


Fig. 3: Overview of the synthesized PMAA-*b*-PS-*b*-PMAA block copolymers (the SI file contains information about the corresponding entries).

of approximately 0.3 for the polymers of entry 8 and 11. This value was also found for the analogues diblock copolymers of PS-*b*-PAA by Kimerling et al. [24] and for block copolymers of PS-*b*-PMAA by Raffa et al. [3]. The polymers with a longer PMAA block have even a higher n value of 0.6–0.8 and show a less shear thinning behavior. An explanation for this phenomena lies in the nature of the aggregates in solution. Polymers with longer hydrophilic blocks form micelles with a larger PMAA corona. This results in stronger interactions between the micelles due to electrostatic forces and entanglement, which are less easily disrupted by shear [23, 27].

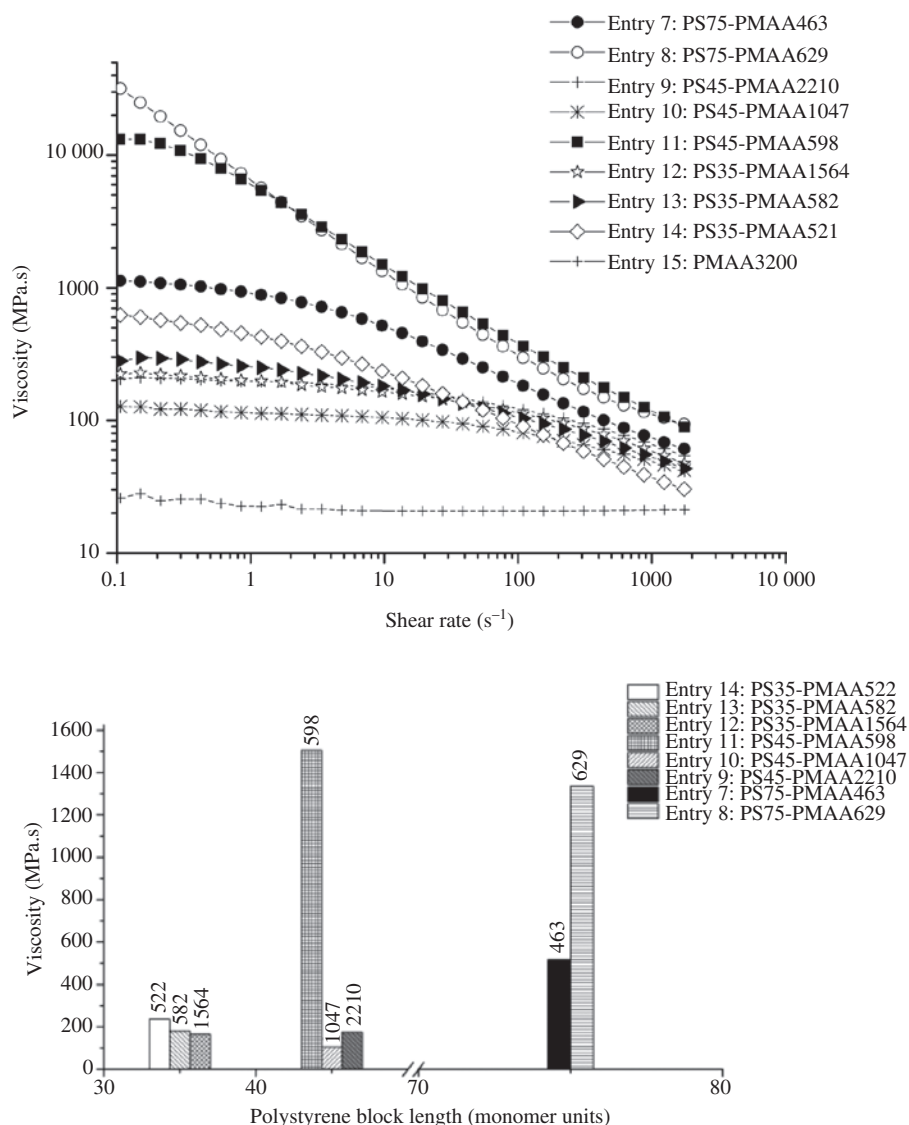


Fig. 4: Viscosity as function of shear rate for different PMAA-PS-PMAA triblock copolymers. Polymers were measured at a concentration of 1wt%. The apparent viscosity (at $\gamma=9.63 \text{ s}^{-1}$; 1 wt%) as a function of the hydrophobic and hydrophilic block length.

In Fig. 4 the apparent viscosity (at $\gamma=9.63 \text{ s}^{-1}$; 1 wt%) as a function of the hydrophobic and hydrophilic block length (in monomeric units) is given. Even if it is difficult to see clear trends in the series, in most cases the viscosity decreases with an increasing hydrophilic PMAA block, as it has been already observed for the corresponding diblock copolymers [23]. It is interesting to note that all the investigated copolymers with the shortest hydrophobic block (35 monomeric units) fail to form strong gels, suggesting that the hydrophobic interactions are weak.

It is also interesting to observe the dependence of the shear viscosity on the concentration for the different systems. In Fig. 5, the apparent viscosity at shear rate 9.63 s^{-1} as a function of the molar concentration is reported. In all cases, sigmoidal curves are obtained. At very low concentrations (the diluted regime [27]), the polymers are non-interacting and form isolated micelles with the hydrophilic block fully stretched into the solution. This is the result of the osmotic pressure exerted by the counter ions trapped in the corona by Coulombic interaction [23]. The stability of the micelles is ensured while the strong hydrophobicity of the core-forming PS overcomes the electrostatic repulsion between the PMAA chains [4]. With an increase in the concentration, the micelles start to interact and the viscosity increases sharply. At even higher concentration,

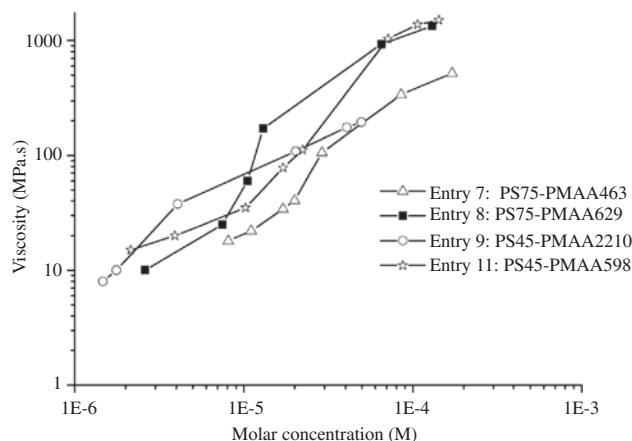


Fig. 5: Apparent viscosity (at shear rate = 9.63 s^{-1}) as a function of the concentration.

the slope of the curve does not increase sharply anymore but remains almost constant. In this region, a sol-gel transition occurs and an interpenetrating polymer network (gel) is formed. It can also be observed that in the concentrated region, the polymers with the shortest PMAA blocks form stronger gels at the same weight concentration. The typical viscosity profile described above is similar to that observed in star and micellar systems [37], for PS-*b*-PAA-*b*-PnBA terpolymers [38] and for PS-*b*-PMAA diblock copolymers [23].

Frequency sweep experiments have been performed to study the characteristics of the triblock copolymer solutions at different concentrations (Fig. 6). Polymers of entry 8 and 11 form viscoelastic gels, with $G' > G''$ over a broad frequency range with a moduli that is nearly independent from the frequency. These two are the only systems, among the ones studied here, which show an apparent yield stress in inversion tests (Fig. 7).

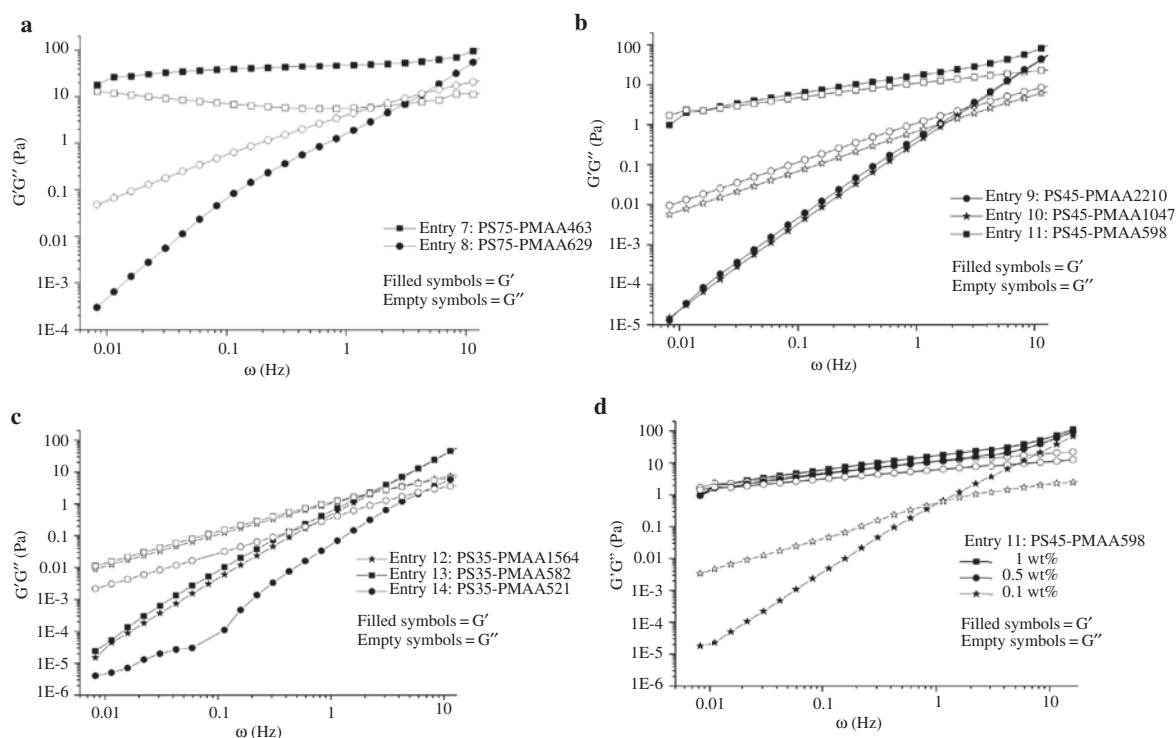


Fig. 6: (a, b, c) G' and G'' vs. the frequency for 1 wt% polymer solutions. (d) G' and G'' vs. the frequency at different polymer concentration for entry 11: PS45-PMAA598.

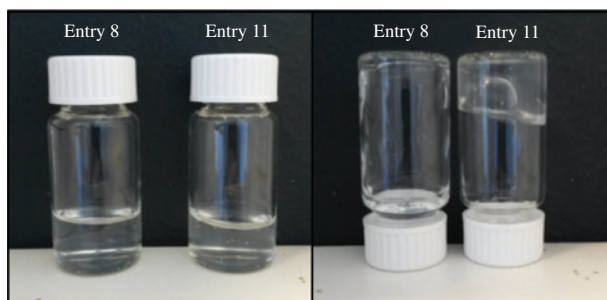


Fig. 7: Tube inversion tests. Concentration = 1 wt%. Entry 8: PS75-PMAA629; Entry 11: PS45-PMAA598.

The polymers with a long PMAA block form viscoelastic solutions in which the dependence of the dynamic modulus from the frequency is more pronounced. This suggests that the polymer network in solution is weak and more easily disturbed.

The viscoelastic behavior between the dilute/semi-dilute (0.1 wt%) and the concentrated regime (1 wt%) can be compared. To do so, cross-over points and phase angle for both concentrations were reported in Fig. 8. In the concentrated regime, the highly viscous solutions (entry 8 and 11) exhibit a high elastic response. The high viscosity results in an increase in both the loss and storage moduli, which indicate the formation of strong gels. In the dilute/semi-dilute regime, the molecular weight (length of the PMAA arms) becomes the controlling factor, because there exist no inner gel network (micelle interaction minimized) thus the elastic

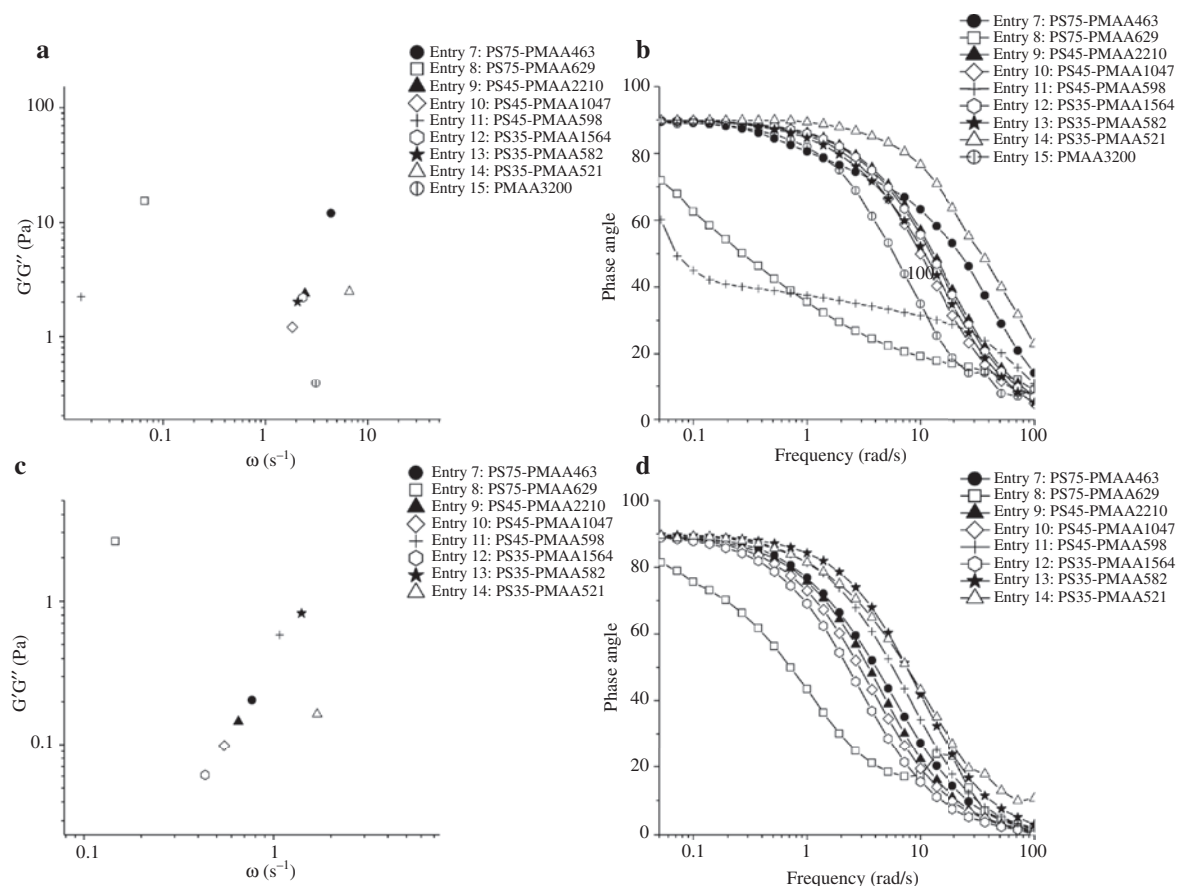


Fig. 8: Cross-over point for the different polymer solutions at G' and G'' vs. the frequency for 1 wt% (a) and 0.1 wt% polymer solutions (c). Phase angle as a function of the frequency at 1 wt% (b) and 0.1 wt% (d) polymer concentration.

response is primarily determined by the length of the hydrophilic block (except entry 8, where the viscosity is still high).

Surface tension

The surface tension (against air) of different polymer solutions was measured using the pendant drop method. None of the amphiphilic triblock copolymers exhibit a CMC. This indicates the presence of kinetically ‘frozen’ micelles and the surface activity is really modest (see SI, Fig. S1). It can be concluded that the studied systems do not show a significant adsorption at the interface and the nature of the aggregates seems to be non-dynamic even for the systems with relatively short hydrophobic blocks (35 styrene units). If any influence can be inferred by these data, the longer the PS block, the more pronounced effect on the surface tension is observed.

The ability of the triblock copolymers to stabilize water/oil emulsions has also been preliminary investigated. Emulsions of crude oil and polymer solutions were stable for a prolonged period of time where the stability was primarily determined by the viscosity, concentration and the molecular structure.

Transmission electron microscopy

The gel structure was also studied by performing electron microscopy, both negative stain EM and cryo-TEM, on solutions at different concentrations. In Fig. 8 negatively stained EM images from 1 wt% solution of the polymers can be seen. The images show a micellar structure where white spots are the spherical hydrophobic cores consisting of polystyrene. The PS core is surrounded by the PMAA hydrophilic corona which is depicted as the dark regions due to penetration of the stain in between the PMAA chains. Due to the high viscosity of the sample multiple layers are often present. The images indicate that polymers with a high viscosity (Fig. 9a–c) have smaller micelles and a more even distribution, indicating a gel network. The images also show that the hydrophilic domains are highly linked together (especially for the polymers with long PMAA chains) which is expected in a gel structure. The gel structure appears disordered in all cases, consistently with previous observations on related block copolymers [39].

Since negative stain TEM is limited in information and prone to over interpretation of the structure of soft materials such as hydrogels, the gel structure of entry 8 (PS75-PMAA629) was also investigated using cryo-transmission electron microscopy in order to have a more native view of the structure [40, 41]. Cryo-TEM images of gels at different concentrations are displayed in Fig. 10. Cryo-TEM observations confirm the results obtained by negative stain, and give no indication of artifacts as a result of the staining method.

The cryo-TEM images show a remarkably ordered gel structure, suggesting that the size distribution of the micelles is narrow. Individual micelles including their core and corona structure can be observed directly from the images. The average radius can be estimated as half of the inter-micellar distance, using the Ruler tool in Adobe Photoshop CS6. It is obtained that the value decreases from around 60 nm to around 50 nm as the concentration goes from 0.3 wt% to 0.5 wt%. We can see how these values compare with predictions that can be made using a simple mathematical model previously developed by Raffa et al. [23], summarized hereafter.

According to the general theory, the gelation of polymeric micellar systems is related to the volume fraction of the micelles, which depends on the molar polymer concentration c , the micelle radius r_{mic} and the aggregation number p according to the following equation [23, 39]:

$$\varphi = \frac{4\pi r_{\text{mic}}^3}{3} \frac{cN}{p} \quad (1)$$

where N is the Avogadro's number. For a block copolymer constituted by N_b units in the hydrophobic block and N_a unit the hydrophilic one, the micellar radius, can be expressed as:

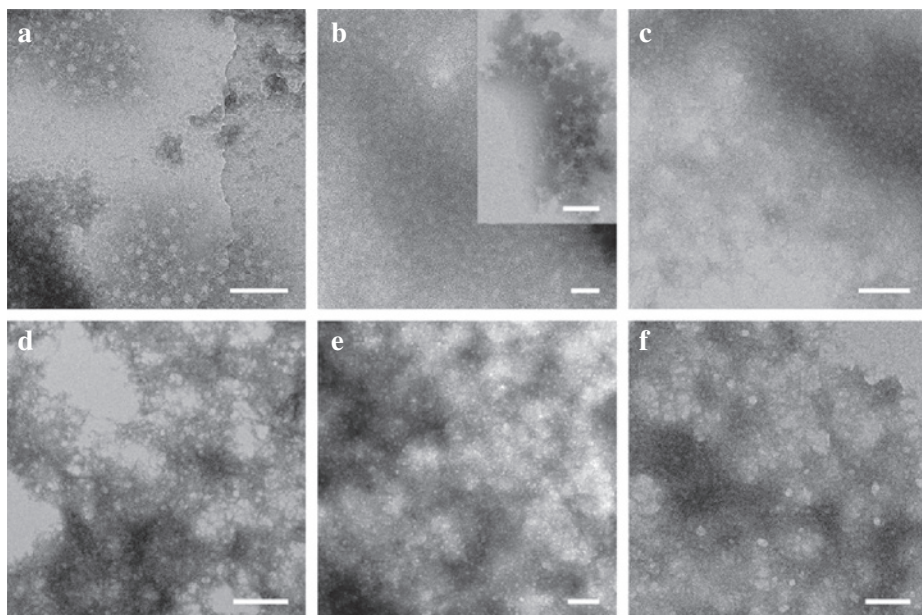


Fig. 9: Negative stain EM pictures of 1 wt% solutions of: entry 7 (a), entry 8 (b), entry 9 (c), entry 10 (d), entry 11 (e) and entry 12 (f). Bars represent 100 nm.

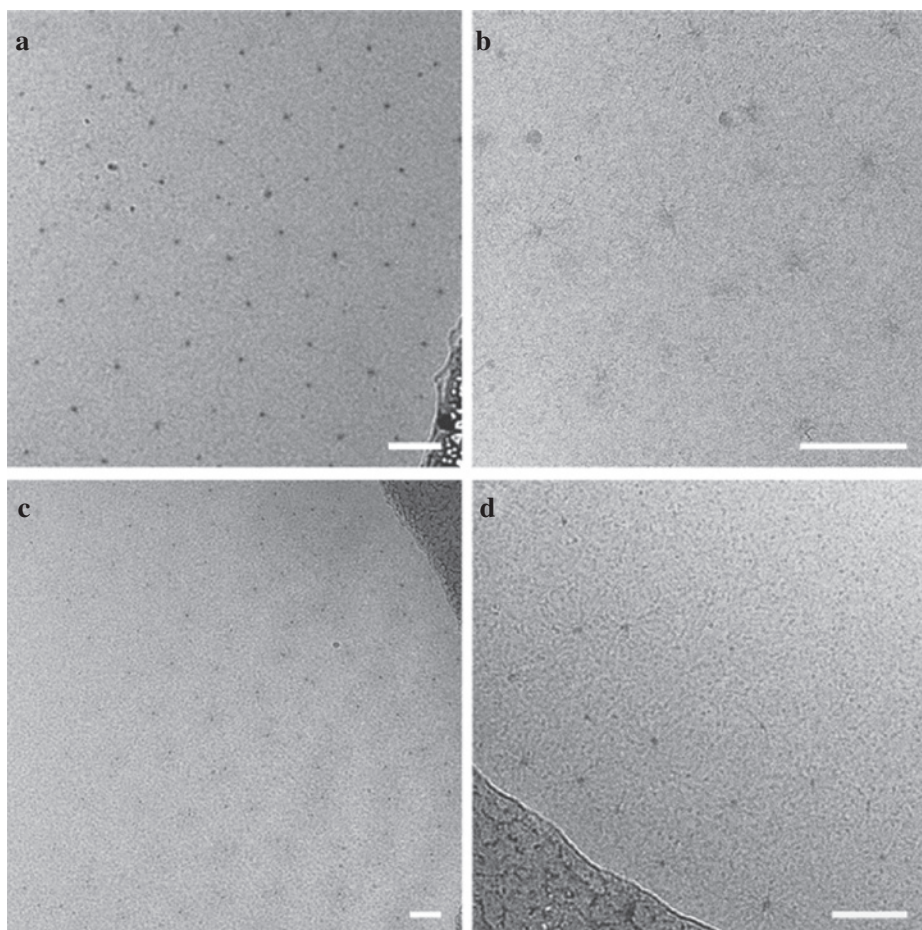


Fig. 10: Cryo-TEM image of an amphiphilic triblock copolymer (entry 8: PS75-PMAA629) at a concentration of 0.3 (a, b) and 0.5 wt% (c, d), respectively. Bars represent 100 nm.

$$r_{\text{mic}} = r_B + r_A = l(pN_B)^{1/3} + lN_A \quad (2)$$

where it is assumed that the micelles have a completely collapsed core and a completely stretched corona and the length of a single monomeric unit (l) is estimated to be 0.25 nm [23]. It has to be noted that the value of N_A for triblock copolymers corresponds to a single hydrophilic arm and consequently a rescaled value $N_A' = N_A/2$ has to be used [3].

In order to estimate the aggregation number, it is assumed that at the concentration where the gelation of the system starts (sharp increase in viscosity), a volume fraction $\varphi = 0.6$ is reached, which is reasonable under certain conditions [39]. Thus, micellar radius and aggregation number for the studied systems can be estimated by combining eqs. 1 and 2. The results are shown in Table 1.

Interestingly, comparing these results with the ones obtained by Raffa et al. [23] using this model for diblock copolymers of PS and PMAA it is possible to observe that the diblock copolymers give much higher aggregation numbers than triblocks, which is in line with the expectation that diblock copolymers arrange into micelles much easier due to less steric hindrance [3, 42]. Focusing on the polymer of entry 8, it is possible to note that for the micellar aggregates observed by cryo-TEM, which are measured at a concentration above the sol-gel transition, the measured corona radius is smaller than the calculated one. The radius in these conditions can be estimated again by the model proposed by Raffa et al. [23] which considers the shrinking of the corona as an effect of the self-contribution of the charged hydrophilic block to the ionic strength of the solution (eq. 3). From Table 2 it can be seen that the calculated values underestimate the measured ones, as it can be also inferred by the low values of volume fractions obtained by using the new radius in eq. 1. Interestingly, the volume fractions obtained by using the measured radii, are both equal to 0.77, which suggests a quite good estimation of the aggregation number.

$$r_{\text{mic}} = l \left[(pN_B)^{1/3} + p^{1/5} (N_A/2)^{3/5} (cN_A)^{-1/5} \right] = l \left[(pN_B)^{1/3} + p^{1/5} N_A^{2/5} c^{1/5} 2^{3/5} \right] \quad (3)$$

pH effect and zeta potential

The rheological properties of the prepared gels proved to be very sensitive to external parameters such as pH and salinity, which makes them promising for applications as responsive hydrogels.

Table 1: Calculated r_A , r_B and p according to eqs. 1 and 2.

Entry	N_B	N_A	Molecular weight (g/mol)	Gel conc. (M) ^a	r_{mic} (nm)	r_B (nm)	r_A (nm)	p
7	75	463	58 638	$3.41 \cdot 10^{-5}$	60.5	2.7	57.9	32
8	75	629	76 708	$1.30 \cdot 10^{-5}$	81.2	2.6	78.6	29
9	45	2210	2 45 904	$8.13 \cdot 10^{-6}$	282.7	6.5	276.3	772
10	45	1047	1 19 211	$1.68 \cdot 10^{-5}$	134.8	3.9	130.9	173
11	45	598	70 210	$1.42 \cdot 10^{-5}$	76.9	2.1	74.8	27
12	35	1564	1 74 548	$1.15 \cdot 10^{-5}$	200.2	4.7	195.5	387
13	35	582	67 536	$2.96 \cdot 10^{-5}$	75.2	2.4	72.8	53
14	35	521	60 872	$3.29 \cdot 10^{-5}$	67.4	2.3	65.1	42

^aPolymer molar concentration. Gel concentration estimated as in Ref. [23].

Table 2: Measured and calculated average radius of a micelle in solution at different concentrations for triblock PS75-PMAA629.

Conc. (wt%)	r_{mic} (nm)	Calc r_{mic} (nm)	φ from SEM	φ Calc
0.5	50	31.9 ^a	0.77	0.18
0.3	60	35.0 ^a	0.77	0.15
0.1	–	81.2 ^b	–	0.6

^aEquation 3. ^bEquation 2.

This could be expected because, as discussed in the introduction, the charged polyelectrolytic PMAA block can stretch or collapse according to its degree of protonation and the ionic strength of the solution.

The zeta potential was measured to study the colloidal stability and the hydrodynamic radius of the self-assembled aggregates as a function of the pH. The magnitudes of the zeta potentials of the studied triblock copolymers are very high and within the range of ± 65 –75 mV. The negative potential indicates that the surface of the particles are negatively charged, as expected from ionized methacrylic acid groups [43]. Systems with the zeta potential in this range exhibit excellent stability of the colloid where the magnitude of the zeta potential indicates the degree of electrostatic repulsion between charged particles [44]. The effect of the pH on the shear viscosity and the zeta potential of a PS-PMAA triblock copolymer solution has been investigated using entry 11: PS45-PMAA598, 70.2 kDa (see Fig. 11). It can be seen that the zeta-potential and viscosity increases with increasing the pH due to ionization of the PMAA blocks. This results in a transition from collapsed to stretched PMAA polymer chains [45] which increases the electrostatic repulsion and subsequently the hydrodynamic radius.

Salt effect

Also the effect of the presence of NaCl on the shear viscosity of 1 wt% PMAA-*b*-PS-*b*-PMAA polymer solutions has been investigated, for the polymer of entry 11 (PS45-PMAA598) at different concentration of NaCl. In Fig. 12, the viscosity versus the shear rate at different NaCl concentrations is shown. The viscosity drops dramatically upon addition of salt. An explanation for this is the fact that the salt ions shield the charges on the PMAA block, which results in chain collapse, shrinking of the corona and weaker intermicellar interactions [3, 24, 25] (see Fig. 13). Correspondingly, this results in a decrease in viscosity and elasticity.

Equation 3 can again be used to model the size of the micelle upon addition of salt. In the regime of high salt concentration, the stretching of the polyelectrolyte arms should disappear due to screening of the charges.

We assume that p is constant because the micelles are ‘frozen’, thus for entry 11, $p = 27$ the results shown in Table 3 are obtained.

The calculations show that the radius of the micelle decreases upon addition of salt. The decreased radius also results in less interaction between the aggregates and subsequently a lower viscosity.

Interestingly, it can be argued that the micelle structure when salt is added is comparable to the gel structure at high polymer concentrations. In both cases, the hydrophilic corona is shrunk. At the gel point, the coronas are interpenetrating and the osmotic effect that stretches the polyelectrolyte brush has disappeared. This can be proved by the fact that the micelle radius as estimated above (5.6 nm) is approximately the same as observed in the negative stain electron microscopy image (see Fig. 8c).

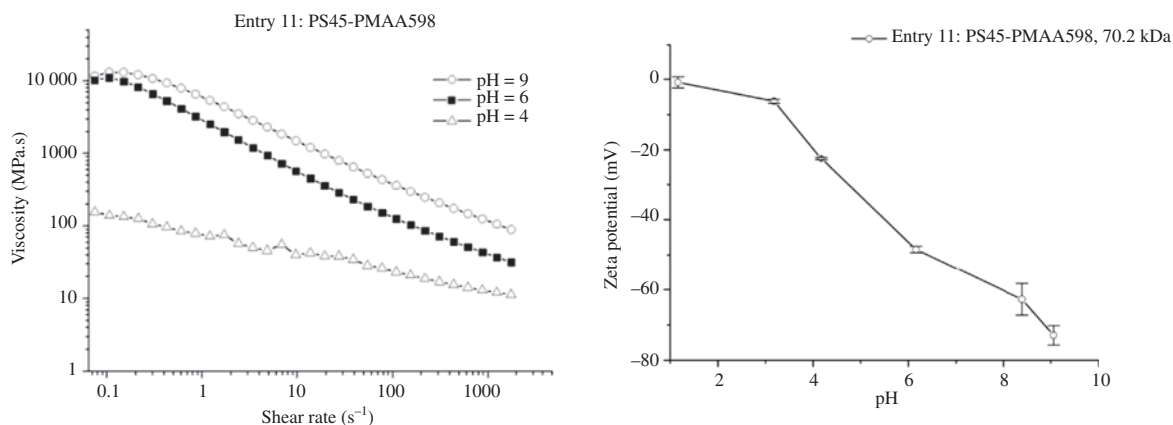


Figure 11: Shear viscosity of entry 11 (PS45-PMAA598, 1 wt%) at different pH and pH dependence of zeta potential of the micelles as a function of the pH for PS45-PMAA598 at 2×10^{-5} M.

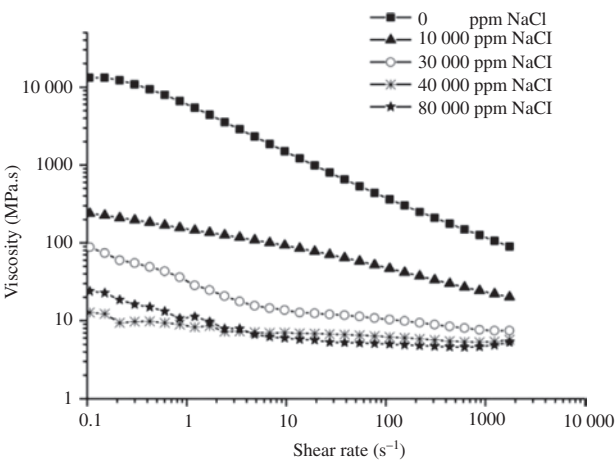


Fig. 12: (a) Shear viscosity of 1 wt% PS45-PMAA598 solutions at different NaCl concentrations.

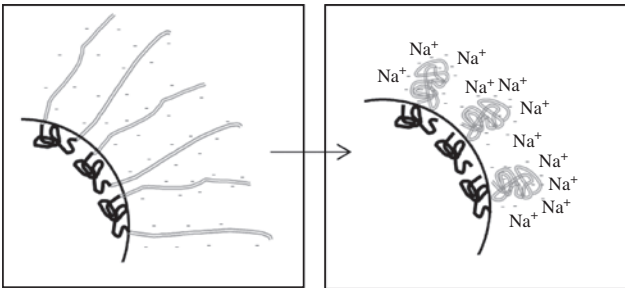


Fig. 13: Star like micelles of triblock copolymer PS-PMAA in water without (left) and with (right) the addition of salt.

Table 3: Micelle radius as a function of salt concentration calculated from eq. 3.

Salt concentration (ppm)	r_{mic} (nm)	ϕ Calc
0	26.29	0.241
10 000	21.50	0.132
30 000	18.48	0.084
40 000	17.67	0.073
80 000	15.81	0.053

Temperature effect

The effect of temperature on the shear viscosity of 1 wt% PMAA-PS-PMAA polymer solutions has been investigated using entry 11: PS45-PMAA598 (see Fig. 14). It can be seen that the viscosity for example at shear rate $\gamma=9.63\text{ s}^{-1}$ hardly decreases. Apparently, the gel structure at 1 wt% is strong enough to resist the breakage of micelles. Moreover, this polymer shows promising thickening capabilities at high temperatures, which is an important requirement for some applications, such as enhanced oil recovery [46].

Conclusion

In this work, well-defined amphiphilic triblock poly(sodium methacrylate)-polystyrene-poly(sodium methacrylate) (PMAA-*b*-PS-*b*-PMAA) copolymers were synthesized by ATRP. The block copolymers were

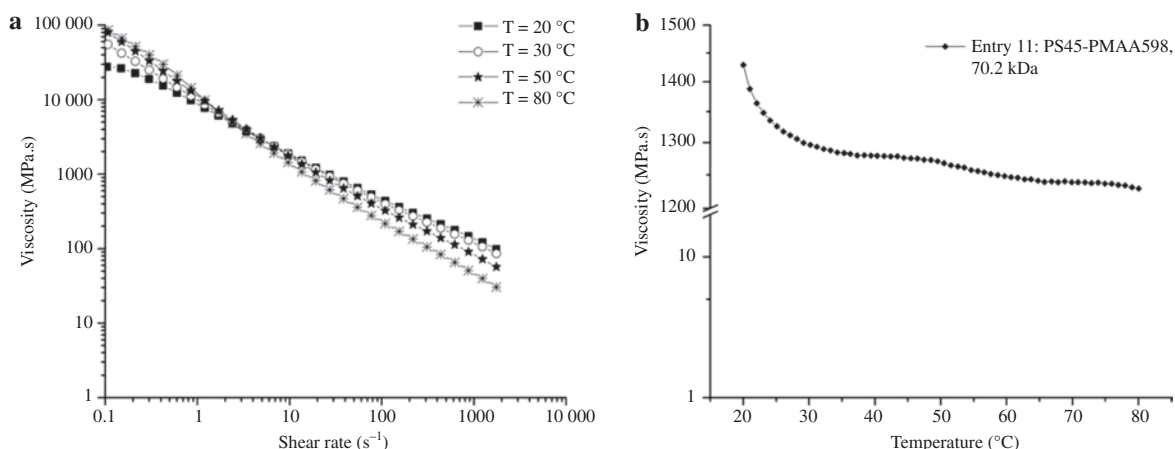


Fig. 14: Shear viscosity of entry 11 (1 wt%, PS45-PMAA598) solutions at different temperatures as function of the (a) shear and the (b) temperature ($\dot{\gamma} = 9.63 \text{ s}^{-1}$).

characterized by a different length of either the hydrophilic or the hydrophobic block to study the influence of the block length on the rheological properties in water. Previous work focused on the rheology of the analogues diblock copolymers of PMAA [23] or PAA [25] and PS, but to the best of our knowledge a systematic study on the effect of the block length on the rheology for triblock copolymers was never considered before.

The obtained triblock copolymers form strong viscoelastic gels depending on the polymer composition. It was found that in the concentrated region (1 wt%) short PMAA block yield the strongest gels. However, polymers with longer PMAA blocks start to form gels at lower concentrations. The hydrophobic block length only plays a minor role until a certain threshold (35 monomeric units) below which the hydrophobic interactions are too weak, resulting in weak gels. Comparable results were found for the analogous PS-*b*-PMAA diblock copolymers [23] where it can be concluded that di- and tri-block copolymers form similar aggregates in solution. It is interesting to observe that regardless the structure (diblock, triblock or star [3]) and the block lengths, the systems always form spherical micelles, with variations only in sizes. It is known that the phase behavior of these systems is very dependent on the sample preparation [47] and it can be very complex, especially if pH, salinity and temperature dependences are taken into account, but a more complete study in this respect is at the moment beyond the scope of this work. What can be concluded for now in this respect is that analogous preparation conditions lead to analogous aggregates morphologies.

The amphiphilic triblock copolymers form star-like micelles in solution. The gel structure was examined by transmission electron microscopy. The images show an ordered micellar structure. The polymers giving a high viscosity at 1 wt% showed smaller micelles and a more even distribution indicating a gel network. A mathematical model that describes the micellar radius was used, showing that it can be used to only qualitatively describe the system. It can be concluded that in the gel structure (high concentration) the PMAA are shrunk due to the screening effect exerted by interpenetrating charged coronas. The aggregation number of the triblock copolymers was estimated to be much lower compared to analogue diblock copolymers, most likely due to more steric hindrance.

The triblock copolymers did not show a significant surface activity and did not exhibit a CMC. It can be concluded that the polymers are present in water as kinetically ‘frozen’ micelles. This is due to the high hydrophobicity and high glass transition temperature of the polystyrene block, which causes a large activation energy barrier for molecular exchange.

Moreover, the influence of the ionic strength, pH and the temperature on the rheology has been preliminary investigated, to explore the potential of these systems for the preparation of smart hydrogels. The experiments showed, as expected, that the pH and ionic strength has a profound influence on the rheology. The viscosity decreased significantly upon addition of salt or decreasing the pH due to shielding of the

charges on the PMAA block, which results in chain collapse, shrinking of the corona and weaker intermicellar interactions. The change in conformation from collapsed to stretched by changing the pH was also quantified with zeta-potential measurements where the zeta-potential increases with increasing the pH due to ionization of the PMAA blocks.

Concluding, a better understanding of the structure-properties relationship of PMAA-*b*-PS-*b*-PMAA amphiphilic triblock copolymers with respect to rheology, which represents the basis of this present work, can provide a useful tool in designing polymers for specific applications for example in the research fields of smart materials and enhanced oil recovery.

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Supplemental Material: The online version of this article (DOI: 10.1515/pac-2016-1021) offers supplementary material, available to authorized users.